Perpendicular magnetic anisotropy in $La_{1-x}Sr_xCoO_{2.5+\delta}/La_{2/3}Sr_{1/3}MnO_3/La_{1-x}Sr_xCoO_{2.5+\delta}$ trilayers (x = 0.05 - 0.5)

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Perpendicular magnetic anisotropy (PMA) of magnetic materials has received much attention because of its potential application to spintronics devices. In general, the tensely strained (001)-La2/3Sr1/3MnO3 (LSMO) layer is easy plane. Here we demonstrate that the tensile LSMO layer will exhibit an out-of-plane magnetic anisotropy if it is sandwiched between two $La_{1-x}Sr_xCoO_{2.5+\delta}$ (LSCO) layers. The most remarkable observation is that the PMA enhances with the increase of the Sr content in LSCO. It is $\sim 2.7 \times 10^6$ erg/cm³ for x = 0.05 and $\sim 4.3 \times 10^{-10}$ 10^6 erg/cm³ for x = 0.5. This value is two orders of magnitude greater than that obtained by compressively straining the LSMO film ($\sim 10^4 \text{ erg/cm}^3$). Analysis of high resolution lattice image shows the formation of perovskite/brownmillerite-type interfaces in the multilayers: Brownmillerite-like lattice structure forms in the interfacial layers of LSCO, resulting in a coherent tilting of adjacent MnO₆ octahedra. This in turn leads to, as evidenced by the analysis of x-ray linear dichroism, selective orbital occupation thus spin reorientation. There is evidence that the brownmillerite-structured LSCO is more easily formed when x is high, which explains the growth of anisotropy constant with the increase of Sr content.

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I. INTRODUCTION

ABO₃-typed transition metal oxides (TMOs) exhibit a wide variety of exotic properties and have been intensively investigated in the past few decades [1–5]. Grouping different perovskite TMOs with coupled charge, spin, and orbital degrees of freedom together to form heterostructures allows a full utilization of interlayer coupling and interfacial reconstruction, presenting a promising approach to explore for unforeseen effects that are important for new conceptual physics and application [6,7]. Advances in this regard are obvious, and numerous emergent phenomena have been reported [8-20]. Among them, the work to tune spin orientation through tilting/distorting oxygen polyhedron near interface is of special interest; in a sense they present a strategy different from traditional magnetoelastic coupling [21,22]. As demonstrated by Liao et al. [19], transmitting the octahedron rotation from NdGaO₃ to $La_{2/3}Sr_{1/3}MnO_3$ (LSMO) caused an in-plane (IP) switching of the easy axis of LSMO by an angle of 90°. The tilting of the interface MnO₆ octahedron has modified the hopping rate of e_g electrons along different axes, thus the magnetic anisotropy. Also by tilting the oxygen octahedra, Kan et al. [20] were able to rotate the easy axis of SrRuO₃ in a film plane by $\sim 45^{\circ}$. These are representative effects of interfacial coupling on the perovskite/perovskite-typed heterostructures.

Since the crystal symmetry and atomic configuration of each constituent of the heterostructures match each other, the interfacial quality of the heterostructures could be very high. However, a similar symmetry combination has a drawback, that is, the orbital reconstruction at interface is usually weak, limiting the exploration space for emergent phenomena.

Recently, Zhang et al. [23] reported perovskite/ brownmillerite-typed heterostructures obtained by grouping LSMO with LaCoO_{2.5+ δ}. The authors found that the easy axis of the LSMO layer aligns along the out-of-plane (OP) direction. There is evidence that local lattice distortion near interface was enhanced since MnO₆ octahedron at the interface has to connect to a CoO₄ tetrahedron. This work presents an alternative approach for the design of artificial materials. However, it remains unaddressed whether this perpendicular magnetic anisotropy (PMA) is limited to the LSMO/LaCoO_{2.5+ δ} combination or a general feature of the perovskite/brownmillerite heterostructures. In this work, we extended the investigation from the LSMO/LaCoO_{2.5+ δ} to the LSMO/La_{1-x}Sr_xCoO_{2.5+ δ} (LSCO, *x* = 0.05–0.5) multilayers. Here partial La³⁺ ions in LCO are replaced by Sr^{2+} in an attempt to modify the ionic state of Co, which is expected to have an effect on the brownmillerite-like phase [24]. We found that the LSMO layer is also perpendicularly anisotropic when sandwiched between two LSCO layers even it is in tensile state. The most remarkable observation is the enhancement of the PMA with the increase of the Sr content in LSCO. From x = 0.05 to 0.5, anisotropic

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constant increases by ~59%. High resolution lattice image shows the formation of perovskite/brownmillerite-typed interfaces and an unusually enhanced tendency towards the brownmillerite phase for the LSCO layer when the content of Sr is high. This work reveals the generality of the PMA in perovskite/brownmillerite multilayers.

II. EXPERIMENTAL PROCEDURES

LSCO(7 nm)/LSMO(5 nm)/LSCO(7 nm) trilayers were grown on TiO₂-terminated (001) – SrTiO₃ single crystal substrates $(3 \times 5 \times 0.5 \text{ mm}^3)$ by the technique of pulsed laser deposition. During sample preparation, substrate temperature was maintained at 700 °C (635 °C) for LSMO (LSCO) and oxygen pressure was fixed to 30 Pa. After deposition, the samples were cooled to room temperature at a rate of 10°C/min in an oxygen pressure of 100 Pa. Five samples with different LSCO layers (x = 0.05, 0.1, 0.2, 0.33, and 0.5) were fabricated for structural and magnetic measurements. Two of them (x = 0.2 and 0.5) were further analyzed by scanning transmission electron microscope (STEM). A [LSCO(4uc)/LSMO(4uc)]₅ superlattice was adopted for the investigation of x-ray absorption spectroscopy (XAS). Here a superlattice was employed to capture the interface effect. As shown later, PMA enhances as the layer thickness of LSMO decreases. A bare LSMO film 5 nm in thickness was also prepared for control measurements of XAS.

Surface morphology of the heterostructures was analyzed by atomic force microscope (SPI 3800N, Seiko). The crystal structure of the samples was determined by a Bruker xray diffractometer equipped with thin film accessories (D8 Discover, Cu $K\alpha$ radiation). Lattice images of the films were recorded by a high-resolution STEM with double C_S correctors (JEOL-ARM200F). Magnetic measurements were performed by a quantum-designed vibrating sample magnetometer (VSM-superconducting quantum interference device.). XAS spectra were collected at the Beam line BL08U1A in the Shanghai Synchrotron Radiation Facility, in the total electron yield mode. Two spectra around the Mn L edge were obtained by setting the incident angle of the linearly polarized x rays to 90° and 30°, respectively (corresponding to E//a and E//c, where E is the electric field of the x ray, a and c are the axes of the sample. The spectra were normalized by a factor so that the L_3 pre-edge and L_2 post edge have an identical intensity for the two polarizations. After that, the pre-edge spectral region was set to zero and the peak at the L_3 edge was set to unity. X-ray linear dichroism (XLD) $(I_{E//a} - I_{E//c})$ is the intensity difference of normalized XAS spectra along two measurement directions, which gives information about empty Mn-3d states, where $I_{E//a}$ and $I_{E//c}$ are the absorption intensities along corresponding directions. The Co L-edge XAS was measured with the incident angle of 90°. The XAS spectra were measured at 300 K.

III. RESULTS AND DISCUSSION

Figure 1(a) is a sketch of the LSCO/LSMO/LSCO trilayers. All samples are of high quality. The film is rather flat. As an example, in Fig. 1(b) we show the surface morphology of LSCO/LSMO/LSCO with x = 0.2. Terrace steps with a



FIG. 1. (a) A sketch of the trilayers grown on (001)-STO substrate. (b) Surface morphology of the LSCO(7 nm)/LSMO(5 nm)/LSCO(7 nm) trilayers (x = 0.2). The film is rather smooth with a root mean square roughness of ~0.2 nm. (c) X-ray diffraction patterns of selected trilayers with x = 0.1, 0.2 and 0.5. Red line is the result of curve fitting, assuming the coexistence of LSMO, La_{0.9}Sr_{0.1}CoO_{2.5} and La_{0.9}Sr_{0.1}CoO₃ phases. (d) Reciprocal space mapping of the ($\overline{103}$) reflection of the trilayers with x = 0.2 and 0.5. The vertical alignment for the reflections from the heterostructures and the substrates (marked by yellow dashed lines) indicates a fully epitaxial growth of the former on the latter, without IP lattice relaxation. Here "MLs" denotes multilayers.

height of one unit cell can be clearly seen. A direct analysis indicates that the root mean square roughness is ~ 0.2 nm. The sharp interfaces are confirmed by low-angle x-ray reflectivity (Fig. S1 in Ref. [25]). Figure 1(c) shows the x-ray diffraction (XRD) spectra for selected LSCO/LSMO/LSCO heterostructures (x = 0.1, 0.2 and 0.5). The XRD pattern is somewhat complex, composed of more than five broad peaks. It is a consequence of the diffraction/interference of the x-ray in the three layers of the sample. The clear multiple XRD peaks are signatures of high crystal quality of the trilayers. As shown by the red curve in Fig. 1(c), curve fitting based on the model of trilayers well produces the experimental results. From curve fitting, the OP lattice parameter can be deduced. It is \sim 3.83 Å for LSMO, ~ 3.75 Å for La_{0.9}Sr_{0.1}CoO₃, and ~ 15.72 Å for La_{0.9}Sr_{0.1}CoO_{2.5}. The perovskite layer exhibits smaller lattice parameters than the corresponding bulk counterpart (~3.87 Å for LSMO and ~ 3.83 Å for La_{0.9}Sr_{0.1}CoO₃). As expected, the film is tensely strained.

To determine the IP lattice parameter, the reciprocal space mappings (RSMs) of the ($\overline{1}03$) reflection of the trilayers were measured. Figure 1(d) presents the RSMs depicted on the [100]-[001] plane for the samples with x = 0.2 and 0.5. Reflections from the film and substrate can be clearly seen. The most remarkable observation is the vertical alignment of the diffraction peaks of the film and the substrate (marked by dashed lines). It means that the film and the substrate share the same IP lattice parameter (a = 3.905 Å). Since the trilayers are very thin (only ~19 nm in total thickness), they



FIG. 2. (a) Thermomagnetic curves of the LSCO/LSMO/LSCO trilayers with x = 0.2, collected in field-cooling mode with an IP or an OP applied field. Red triangles mark the temperature for spin reorientation. (b) and (c) Magnetic moment as a function of applied field, extracted from the data of (a). The corresponding temperatures are T = 10 and 140 K. Shaded area is the energy required to orientate magnetic moment from the OP to the IP direction. (d) Anisotropy constant as a function of temperature. Values marked by red squares were calculated from directly measured magnetic loops.

are fully strained, without lattice relaxation. Similar results are obtained for other trilayers investigated.

As demonstrated above, the trilayers are in a tensile state. For a tensely strained LSMO film, the magnetic moment will align in the film plane due to magnetoelastic coupling [21,22]. This is exactly what has happened to a bare LSMO film (Fig. S2 in Ref. [25]). When sandwiched between two LSCO layers, however, the LSMO layer undergoes a dramatic spin reorientation; instead of lying in film plane, the magnetic moment of LSMO aligns perpendicularly to the film plane. Figure 2(a) shows the thermomagnetic curves (M-T) of LSCO/LSMO/LSCO (x = 0.2), acquired in the field-cooling mode with IP and OP applied fields, respectively. Here x was set to 0.2 since the corresponding LSCO film grown on (001) STO is nonmagnetic [26], i.e, magnetic signals come exclusively from LSMO. With the decrease of temperature, the magnetic moment undergoes first an obvious increase at the Curie temperature (T_C) of the LSMO layer and then a sudden drop when measured along the IP direction. Accompanying the latter process, the OP component of the magnetic moment exhibits a concomitant growth. Although the IP and OP M-Tcurves approach each other as the magnetic field increases, an inflection can still be clearly seen in the IP M-T curve up to the field of 1.5 T. Notably, anomalous spin reorientation was also observed in $La_{1-r}Sr_rCoO_3/LSMO/La_{1-r}Sr_rCoO_3$ trilayers on LaAlO₃ substrates [27]. In that case the spin prefers to align along IP rather than OP direction.

To quantify the PMA, we estimated the anisotropy constant (K) for the trilayers. Figures 2(b) and 2(c) present the magnetic moment as a function of applied field (M-H), extracted

from the M-T curves in Fig. 2(a) at two typical temperatures of 10 and 140 K. Along the OP direction, the magnetic moment increases rapidly with applied field, and saturates in a field about 0.1 T. Further increase in magnetic field only leads to a very slow magnetic growth. Along the IP direction, in contrast, the magnetic moment exhibits a slow growth with applied field, without signatures of saturation up to the field of 2.5 T. These features are also observed at other temperatures. An increase in temperature leads to a reduction in saturation of the magnetic moment, without affecting the general M-H dependence. It is easy to see that the energy required to orientate the magnetic moment from the OP to the IP direction equals the area encircled by the two M-H curves (shaded area). A direct calculation yields an output of K $\sim 4 \times 10^6$ erg/cm³ at 10 K. This PMA is comparable to that of CoCrPtX which is the medium for perpendicular recording ($\sim 2 \times 10^6 \text{ erg/cm}^3$) and much stronger than that of a compressively strained LSMO/LaAlO₃ film (K $\sim 10^4 \text{ erg/cm}^3$) [28,29].

Following the same procedure, the anisotropy constants at other temperatures were also calculated. As shown in Fig. 2(d), *K* takes high values around $\sim 4 \times 10^6$ erg/cm³ from 10 to 100 K, and decreases gradually as temperature increases from 100 to 200 K. It changes sign at ~ 240 K, indicating a transition to the easy plane state, the normal state of a tensile LSMO film. The anomalous PMA at low temperatures is further confirmed by directly measuring magnetic loops with IP and OP applied fields, respectively (Fig. S3 in Ref. [25]). As shown in Fig. 2(d), the deduced anisotropy constant (red symbols) agrees well with those presented here.

In a previous work [23], PMA has already been observed in the LaCoO_{2.5+ δ}/LSMO/LaCoO_{2.5+ δ} multilayers. It, therefore, could be a general feature of the multilayers based on cobalt oxides. Indeed, PMA is also observed in LSCO/LSMO/LSCO trilayers other than x = 0.2. More than that, it is strongly dependent on the Sr content of LSCO. Figure 3(a) illustrates the thermomagnetic curve for the LSCO/LSMO/LSCO trilayers with different Sr content. For clarity, here only the data collected under a fixed field of 0.01 T were shown for each sample. From first glance, the IP curve deviates progressively from the OP one as x sweeps from 0.05 to 0.5, i.e., the tendency towards PMA enhances as x increases. When x is 0.05, as shown in Fig. 3(a), magnetic alignment remains in the film plane when magnetic order sets in at T_C , and it transitions to the OP direction only below 204 K. However, OP orientation prevails below \sim 264 K when x = 0.5.

In fact, *M*-*T* curves in different fields are also obtained for different samples (Fig. S4 in Ref. [25]). Based on these results, the anisotropy constant is calculated. In Fig. 3(b) we show the dependence of *K* on *x*. We take the result of T = 10K as an example. As *x* sweeps from 0.05 to 0.2, the anisotropy constant grows from 2.7×10^6 erg/cm³ to 4.0×10^6 erg/cm³, increased by 48%. Around x = 0.2, an obvious kink emerges in the *K*-*x* curve, leading to a considerable declining of the *K*-*x* slope. However, *K* keeps growing up to the content of x = 0.5. These are general features of the effect of Sr content, also observed in other *K*-*x* curves obtained at high temperatures. Well above the spin reorientation temperature, however, *K* takes negative values and is weakly *x*



FIG. 3. (a) Thermomagnetic curves of the LSCO/LSMO/LSCO trilayers, collected in the field-cooling mode with an IP or an OP applied field of 0.01 T. (b) Anisotropy constant as a function of Sr content in LSCO, obtained at three representative temperatures of 10, 150, and 280 K. Inset sketches mark the spin direction. Solid lines are guides for the eye.

dependent, indicating a return to the IP direction of the magnetic moment.

As demonstrated above, the LSMO sandwiched between two LSCO layers displays an anomalous PMA even as is tensely strained, in sharp contrast to the bare LSMO film. To check what has happened to LSCO/LSMO/LSCO, spectra XAS was collected for the [LSCO(4uc)/LSMO(4uc)]₅ superlattice with x = 0.33, where the LSCO and LSMO layers are very thin to highlight interfacial effect. As shown in Fig. S5 in Ref. [25], PMA enhances as the layer thickness of LSMO decreases. x was set to 0.33. In this case, superlattices are of high quality. Macroscopic measurement indicates that this sample exhibits the typical PMA feature (Fig. S6 in Ref. [25]). As will be seen later, the magnetic contributions come mainly from the LSMO layer in multilayers. Hence we only present the L_2 and L_3 absorption peaks of Mn here. The experiments have been conducted at 300 K to avoid the interference of ferromagnetic signals [30].

Figures 4(a) and 4(b) show the normalized XAS spectra for the samples of LSMO(5 nm)/STO and [LSCO(4uc)/LSMO(4uc)]₅/STO, respectively. From a first glance, the spectra obtained with parallel (E//a, $I_{E//a}$) and perpendicular (E//c, $I_{E//c}$) optical polarizations are similar, where $I_{E//a}$ and $I_{E//c}$ are the intensities of the IP and OP absorption peaks, respectively. However, a careful analysis indicates the existence of considerable difference. As



FIG. 4. (a) Normalized Mn-XAS spectra for a bare LSMO(5 nm) film and (b) the [LSCO(4uc)/LSMO(4uc)]₅ superlattices, measured with the optical polarization parallel $(E//a, I_{\rm IP})$ or perpendicular $(E//c, I_{\rm OP})$ to film plane. The deduced XLD spectrum is also shown in the bottom panels of the corresponding figures. Shaded XLD peaks provide information on orbital occupancy. The inset sketches mark the spin orientation of the LSMO layer.

shown by the XLD spectra defined by $(I_{E//a} - I_{E//c})$ (bottom panels of Fig. 4), the XLD spectrum displays a dramatic variation from the LSMO film to the [LSCO/LSMO]5 superlattices: it transits from negative to positive peak around the $Mn - L_2$ edge. As well documented, the integration of the XLD spectrum around the L_2 edge (648.5–660 eV) gives a direct measurement for empty Mn 3d states, proportional to the relative occupancy of the $d_{x_2-y_2}$ and $d_{3z_1^2-r_2}$ orbital states [30-32]. Positive (negative) value means a preferential occupation of the $d_{3z^2-r^2}$ ($d_{x^2-v^2}$) orbital [30–32]. According to Fig. 4(a), the XLD peak is negative, i.e., the low-lying orbital is $d_{x^2-y^2}$ for bare LSMO. This is understandable noting that the MnO₆ octahedron has been expanded along the film plane by tensile strains [30]. A direct calculation indicates that the orbital momentum is finite in this case, lying in the IP direction [33]. On the contrary, the low lying orbital is $d_{3r^2-r^2}$ for the superlattice. This is an observation that it is $d_{3z^2-r^2}$ rather than $d_{x^2-y^2}$ that is preferentially occupied for the tensile LSMO film. It is easy to prove that in this case the orbital momentum aligns in the direction perpendicular to film plane [33]. According to Bruno [34,35], the easy axis prefers to take the direction of orbital momentum. In this picture, we can understand why the bare LSMO is easy plane whereas the LSCO/LSMO/LSCO trilayers, which are a special form of superlattice, are perpendicularly anisotropic.

To address how preferred orbital occupancy occurs for superlattice and how the content of Sr in LSCO takes effect, the lattice structures of the LSCO/LSMO/LSCO trilayers with x = 0.2 and 0.5 are further studied based on the technique of STEM. Figures 5(a) and 5(b) present the typical high-angle annular dark-field (HAADF) images of the cross section of the LSCO /LSMO/LSCO trilayers, acquired along the [110] zone axis. The brighter and fainter spots correspond to the La/Sr and Mn/Co atomic columns, respectively. The most remarkable observation is the structure modulation in the LSCO layer, as demonstrated by the appearance of parallel dark stripes. This feature is especially obvious in the top LSCO layer, where a dark stripe appears every other row. A similar lattice structure has been observed in the LaCOQ_{2.5+ δ} layer of



FIG. 5. (a) and (b) Typical HAADF images of the cross section of the LSCO(7 nm)/LSMO(5 nm)/LSCO(7 nm) trilayers for x = 0.2(a) and 0.5 (b), recorded along [110] zone axis. Yellow arrows mark the LSCO/LSMO interface. Red arrows denote dark stripes in LSCO. Inset image in (b) is an enlarged view to show the breath mode lattice distortion (marked by red dots). (c) HAADF image of LSCO/LSMO/LSCO with x = 0.5, obtained along [010] zone axis, and the corresponding line profile along the vertical Co/Mn column. It clearly shows a sharp LSMO/LSCO interface (marked by a yellow line). (d) Structure model of perovskite/brownmillerite heterostructure viewed along [110] zone axis. (e) Normalized Co-XAS spectra for the LSCO/LSMO/LSCO trilayers with different Sr contents.

the LaCoO_{2.5+ δ}/LSMO/LaCoO_{2.5+ δ} multilayers and ascribed to the formation of the brownmillerite-like phase [23]. Indeed, breath mode lattice distortion for the Co ions in dark stripes, which is a fingerprint of the brownmillerite phase [36–39], is observed in the LSCO layer in both samples [enlarged image in Fig. 5(b) and schematic diagram in Fig. 5(d)]. A further finding is that the brownmillerite phase prefers to appear when the content of Sr is high. As shown in Figs. 5(a) and 5(b), both the top and bottom layers exhibit the modulation structure with a periodicity of $2a_0$ for the sample with x = 0.5 whereas the dark stripes with $2a_0$ and $3a_0$ are observed in the LSCO layer for the sample of x = 0.2, where a_0 is the lattice constant of the corresponding perovskite unit cell. More than that, dark stripes prefer to appear near interfaces, which is similar to the LaCoO_{2.5+ δ}/LSMO multilayers [23]. As shown by line profile analysis in Fig. 5(c) (averaged over six vertical Mn/Co columns), the Co columns in dark stripes are weaker in intensity than the Mn ones, and the first dark Co-O layer locates just above the Mn-O layer. In this case, the MnO₆ octahedra in the interfacial layer connect to CoO₄ tetrahedra (dark strips) rather than CoO_6 octahedra, elongating along the c axis to reduce elastic energy as shown by Zhang *et al.* in Ref. [23]. This in turn leads to a lift of the energy level of $d_{x^2-y^2}$ with respect to that of $d_{3z^2-r^2}$. Also, a charge transfer from Mn to Co ions may take place, which will further stabilize the $d_{3z^2-r^2}$ orbital. All these explain the preferred occupancy of the $d_{3z^2-r^2}$ orbital even when LSMO is in tensile state. According to STEM, the interfacial brownmillerite phase induces a unique MnO₆ distortion that favors PMA. A natural inference is that the tendency to PMA for the multilayer will be strongly dependent on the amount of brownmillerite phase. Since the proportion of the brownmillerite phase grows with the content of Sr in LSCO, the anisotropy constant increases with *x*.

Since only local lattice image can be obtained by STEM, further evidence is required to show the increase of the proportion of the brownmillerite LSCO phase with the content of Sr. In fact, the XRD spectrum contains all information about each layer of the samples. By assuming the coexistence of $La_{1-x}Sr_xCoO_{2.5}$, $La_{1-x}Sr_xCoO_3$, and $La_{2/3}Sr_{1/3}MnO_3$ layers, we calculated the XRD spectra. Fixing $La_{2/3}Sr_{1/3}MnO_3$ at 5 nm, we satisfactorily reproduced the experimental results by adjusting the relative thickness of $La_{1-x}Sr_xCoO_{2.5}$ and $La_{1-x}Sr_xCoO_3$ to an optimal ratio. Based on these calculations, the proportion of the brownmillerite phase can be determined as a function of *x*. As expected, it shows a monotonic increase as *x* grows (Fig. S7 in Ref. [25]).

To get further information on the effect of Sr on the valence state of Co ions, in Fig. 5(e) we show the XAS spectra of the Co L_2 and L_3 peaks. The L_3 peak slightly shifts to low energies as x sweeps from 0.05 to 0.33 (the maximal energy reduction is ~0.26 eV). As is well established, this is an indication for the decrease in the valence state of Co. It is in conflict with our expectation that the incorporation of Sr may lead to an increase in the valence of Co ions. This could be a consequence of enhanced oxygen loss in the LSCO layer after Sr is introduced. This result is consistent with the results of XRD and STEM, i.e., the proportion of brownmillerite phase grows as x increases. This conclusion is also confirmed by the analysis of the x-ray photoelectron spectroscopy of LSCO/LSMO/LSCO (Fig. S8 in Ref. [25]).

By fabricating perovskite/brownmillerite multilayers on SrTiO₃ substrates we stabilize the $d_{3z^2-r^2}$ orbital of the MnO₆ octahedra. As a result, the spin orientation experiences an IP to OP transition. This is different from the work of Zhang *et al.* [27] about the perovskite/perovskite heterostructures on LaAlO₃. In that case, the IP anisotropy prevails due to the interlayer coupling causing an off center shift of Mn ions in LSMO.

In fact, there have been intensive investigations on the effect of interlayer coupling in the past few years. By sandwiching $La_{0.7}Sr_{0.3}MnO_3$ between two $La_{0.7}Sr_{0.3}CrO_3$ layers, Koohfar *et al.* [40] found that the $La_{0.7}Sr_{0.3}MnO_3$ film remains quite ferromagnetic down to the thickness of two unit cells, which is obviously different from the bare layer counterpart. The $La_{0.7}Sr_{0.3}CoO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ combination was also investigated. Li *et al.* [41,42] reported that interfacial layer of $La_{0.7}Sr_{0.3}CoO_3$ became a soft ferromagnetic when it was grouped together with $La_{0.7}Sr_{0.3}MnO_3$. Although these works vividly demonstrated the unusual effect of interlayer coupling on manganite, the effect of heterostructure on magnetic anisotropy was not investigated.

Finally, we would like to emphasize that the PMA is determined by the LSMO layer of the multilayers. We found that the saturation magnetization is nearly constant for our samples with different LSCO layers (Fig. S9 in Ref. [25]). The maximal magnetization is $3.71 \,\mu_B/\text{Mn}$, gained when x = 0.5. The minimal magnetization is $\sim 3.48 \,\mu_B/\text{Mn}$, gained when x = 0.2. It has been reported that LSCO is nonmagnetic when x = 0.2. If LSMO accounts for $3.48 \,\mu_B/\text{Mn}$, the contribution from the LSCO layer is at most 6% of the total magnetization $(3.71 \,\mu_B/\text{Mn})$. Possibly, the LSCO layers crystalize in the brownmillerite phase, which has no ferromagnetic order or is weakly magnetic.

IV. CONCLUSIONS

Atomic level controlled LSCO/LSMO/LSCO heterostructures have been fabricated on STO substrates and perpendicular magnetic anisotropy has been observed even when the heterostructure is tensely strained. The most remarkable observation is the enhancement of the perpendicular anisotropy with the increase of the Sr content in LSCO. The maximal anisotropy constant is $\sim 4.3 \times 10^6$ erg/cm³, gained when x = 0.5. According to the analysis of high resolution lattice image, LSCO prefers to crystalize in the brownmillerite phase when the content of Sr is high. The brownmillerite phase causes, as evidenced by the result of the x-ray linear dichroism, an orbital reconstruction of the MnO_6 octahedra, thus the reorientation of the preferred magnetic direction.

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